

# The influence of the density of the solvent on the static and dynamic properties of star polymers. A molecular dynamics study

B. Smit,<sup>a)</sup> A. van der Put, C. J. Peters, and J. de Swaan Arons

*Laboratorium voor Anorganische en Fysische Chemie, Technische Universiteit Delft, Delft, The Netherlands*

J. P. J. Michels<sup>b)</sup>

*van der Waals Laboratorium, Universiteit van Amsterdam, P. O. Box 20216, 1000 HE Amsterdam, The Netherlands*

(Received 8 October 1987; accepted 26 October 1987)

The static and dynamic properties of a star polymer in a solvent at several densities have been studied by computer simulations using molecular dynamics. In addition to the repulsive Lennard-Jones potential which interacts between all particles we have used a harmonic potential to link 19 particles into a star polymer. It was found that both the static properties (e.g., the end-to-end distance and the radius of gyration) as well as the dynamic properties (e.g., the autocorrelation functions and the center-of-mass diffusion coefficient) are significantly influenced by the density of the solvent.

## I. INTRODUCTION

Systems of large molecules in a solvent of small molecules are encountered in many technical applications, e.g., supercritical extraction and retrograde condensation.<sup>1</sup> One of the problems in the description of these systems is to incorporate changes of the configurations of the molecules in an equation of state. Computer simulations of model systems may provide some insight into this problem.

Over the past few years several simulation methods and models have been used to study linear polymers<sup>2-9</sup> and ring polymers.<sup>10</sup> In this study, the properties of a star polymer in a solution of monomers at several densities are considered. Structures like star polymers can be found in many forms such as branched alkanes, triglycerides, etc., and are the topic of many experimental studies.<sup>11</sup>

To our knowledge, star polymers have been used in computer simulations only to study entanglements effects.<sup>12,13</sup> The influence of the solvent on the properties of linear polymers has been investigated in several molecular dynamics studies. Bruns and Bansal<sup>2,3</sup> found that the static properties of the polymer are influenced by the solvent. The data generated by Bishop *et al.*<sup>4-6</sup> and Rapaport<sup>7,8</sup> showed that the solvent had almost no effect on these properties. These observations have been confirmed in a recent study by Khalatur *et al.*,<sup>9</sup> in which they concluded that the behavior of a chain immersed in a monomeric solvent is mainly determined by intrachain rather than by solvent effects.

From an intuitive point of view these results are rather remarkable. Therefore more simulations have been performed in order to study the influence of the solvent on some properties of polymers in more detail.

## II. MODEL AND COMPUTATIONAL DETAILS

In this study we have used a single star polymer of 19 segments with 3 branches of 6 segments connected to a cen-

tral monomer. The star polymer is immersed in a solvent of 481 monomers.

The interatomic potential in our model consists of two parts: a shifted Lennard-Jones potential which operates between all the 500 particles and a harmonic potential which links the first 19 monomers into a star polymer. The Lennard-Jones potential is given by

$$U^{LJ}(r) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] + \epsilon, & r \leq 2^{1/6}\sigma \\ 0, & r > 2^{1/6}\sigma \end{cases} \quad (1)$$

and the harmonic potential is given by

$$U_{ij}^H(r) = \frac{k}{2} (|r_j - r_i| - \sigma)^2 \quad (2)$$

for

$i = 2, \dots, 6$  and  $j = i + 1$  (branch 1),

$i = 8, \dots, 12$  and  $j = i + 1$  (branch 2),

$i = 14, \dots, 18$  and  $j = i + 1$  (branch 3),

$i = 1$  and  $j = 2, 8, 14$  (central monomer).

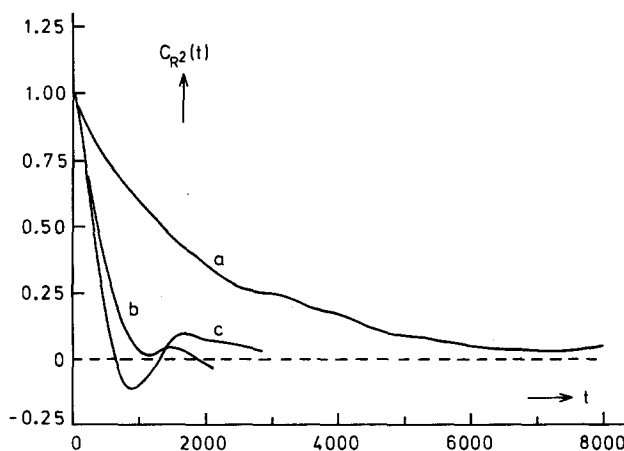


FIG. 1. Autocorrelation function for the square end-to-end distance at several densities. (a)  $\rho^* = 0.80$ ; (b)  $\rho^* = 0.30$ ; (c)  $\rho^* = 0.05$ .

<sup>a)</sup> Present address: Koninklijke/Shell-laboratorium, Amsterdam (Shell Research B. V.) P. O. Box 3003, 1003 AA Amsterdam, The Netherlands.

<sup>b)</sup> Author to whom correspondence should be sent.

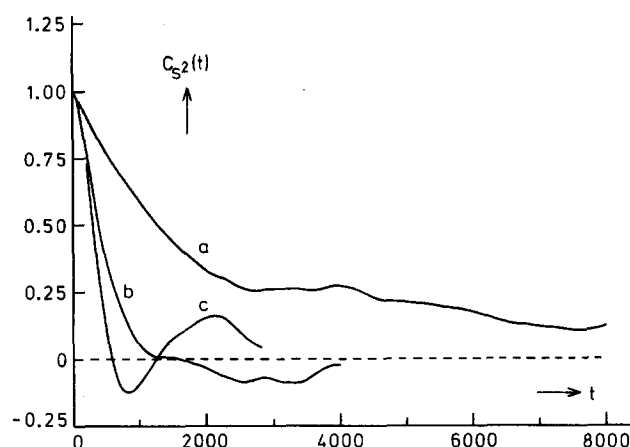


FIG. 2. Autocorrelation function for the square radius of gyration at several densities. (a)  $\rho^* = 0.80$ ; (b)  $\rho^* = 0.30$ ; (c)  $\rho^* = 0.05$ .

The value of the force constant  $k$  is made sufficiently large such that 98% of the connected units have a momentary length with 2% of the average value  $s$ .

Throughout this paper reduced units are used. In these, lengths are measured in units  $\sigma$ , velocity in units  $(\epsilon/m)^{1/2}$ , and time in units  $\tau_0 = \sigma/(m\epsilon)^{1/2}$ .

Periodic boundary conditions are imposed in all three directions. The equations of motion are solved with Verlet's integration scheme.<sup>14</sup> Tests on the time step showed that  $\Delta t = 0.007 \tau_0$  was appropriate. No significant drift of the temperature and total energy occurred during the simulation.

Once thermal equilibrium has been established, the successive configurations of the polymer on equally spaced times are stored for further analysis.

For comparison we also performed a simulation for an isolated polymer, thus without the 481 monomers. This can be regarded as the limiting case at zero density.

### III. RESULTS

Some important static properties of a star polymer are: the end-to-end distance  $R$ ; end-to-midpoint distance  $M$ ; and radius of gyration  $S$ . These properties at time  $t$  are given by the following relations:

$$R^2(t) = \frac{1}{3} \{ |\mathbf{r}_{B_1}(t) - \mathbf{r}_{B_2}(t)|^2 + |\mathbf{r}_{B_1}(t) - \mathbf{r}_{B_3}(t)|^2 + |\mathbf{r}_{B_2}(t) - \mathbf{r}_{B_3}(t)|^2 \}, \quad (3)$$

$$M^2(t) = \frac{1}{3} \{ |\mathbf{r}_{B_1}(t) - \mathbf{r}_1(t)|^2 + |\mathbf{r}_{B_2}(t) - \mathbf{r}_1(t)|^2 + |\mathbf{r}_{B_3}(t) - \mathbf{r}_1(t)|^2 \}, \quad (4)$$

$$S^2(t) = \frac{1}{N_p} \sum_{j=1}^{N_p} |\mathbf{r}_j(t) - \mathbf{Z}(t)|^2 \quad (5)$$

with

$N_p$ : number of polymer segments ( $N_p = 19$ );

$\mathbf{r}_{B_i}$ : position of the last segment of a branch of the star polymer ( $B_1 = 7, B_2 = 13, B_3 = 19$ );

$\mathbf{r}_1$ : position of the central segment;

$\mathbf{r}_j$ : position of the  $j$ th segment of the polymer;

$\mathbf{Z}(t)$ : center of mass

$$\mathbf{Z}(t) = \frac{1}{N_p} \sum_{j=1}^{N_p} \mathbf{r}_j(t). \quad (6)$$

The instantaneous shape of a star polymer is characterized by the three principal orthogonal components of  $S^2$ ,  $0 \leq R_i^2 \leq R^2 \leq R_i^2$ . These components are obtained from the eigenvalues of the inertia tensor  $T^{ab}$ . The value of this tensor is denoted by

$$T^{ab}(t) = \frac{1}{N_p} \sum_{j=1}^{N_p} [\mathbf{r}_j(t) - \mathbf{Z}(t)]_a [\mathbf{r}_j(t) - \mathbf{Z}(t)]_b. \quad (7)$$

$a$  and  $b$  indicate two directions in a Cartesian frame.

The mean square end-to-end distance  $\langle R^2 \rangle$ , end-to-midpoint distance  $\langle M^2 \rangle$ , radius of gyration  $\langle S^2 \rangle$ , and the three eigenvalues of the inertia tensor  $\langle R_i^2 \rangle$  are calculated with the general relationship

$$\langle A^2 \rangle = \frac{1}{N_m} \sum_{j=1}^{N_m} A^2(j) \quad (8)$$

with

$N_m$ : total number of samples,

where  $A(j)$  represents the value of  $R, M, S$ , and  $R_i$  at equally spaced time steps with length  $n_0$ .

TABLE I. The static properties of a star polymer in a solvent.  $\rho^*$  denotes the reduced density ( $\rho^* = \rho\sigma^3$ );  $T$  the reduced temperature ( $T^* = Tk/\epsilon$ ).

$nr$	$\rho^*$	$T^*$	$N_m \times 10^{-3}$	$n_0$	$\langle R^2 \rangle$	$\langle M^2 \rangle$
1	0	1.98	200	1000	$29.73 \pm 1.26$	$12.63 \pm 0.56$
2	0.05	2.00	160	800	$27.48 \pm 0.82$	$11.76 \pm 0.26$
3	0.30	2.00	200	2000	$25.82 \pm 1.20$	$11.38 \pm 0.63$
4	0.60	2.02	400	4000	$24.72 \pm 1.03$	$11.22 \pm 0.31$
5	0.80	2.01	840	10000	$23.06 \pm 1.73$	$10.27 \pm 0.77$
$nr$	$\langle S^2 \rangle$	$\langle R_1^2 \rangle / \langle S^2 \rangle$	$\langle R_2^2 \rangle / \langle S^2 \rangle$	$\langle R_3^2 \rangle / \langle S^2 \rangle$		
1	$5.43 \pm 0.18$	$0.062 \pm 0.003$	$0.271 \pm 0.013$	$0.667 \pm 0.040$		
2	$5.12 \pm 0.09$	$0.064 \pm 0.005$	$0.261 \pm 0.010$	$0.675 \pm 0.021$		
3	$4.89 \pm 0.08$	$0.069 \pm 0.007$	$0.279 \pm 0.020$	$0.652 \pm 0.016$		
4	$4.68 \pm 0.09$	$0.067 \pm 0.008$	$0.275 \pm 0.020$	$0.657 \pm 0.011$		
5	$4.42 \pm 0.11$	$0.070 \pm 0.006$	$0.255 \pm 0.020$	$0.675 \pm 0.042$		

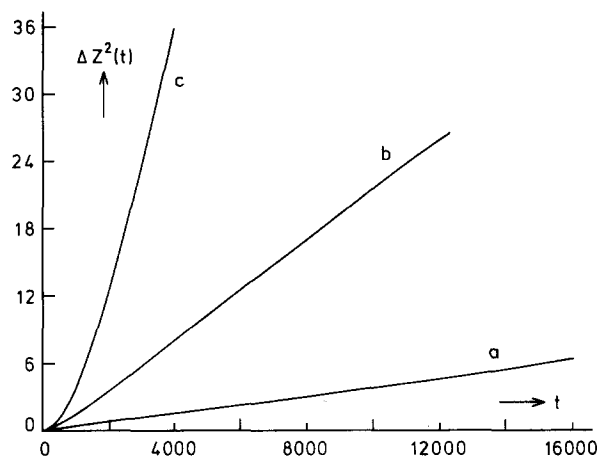


FIG. 3. Mean square center-of-mass displacement. (a)  $\rho^* = 0.80$ ; (b)  $\rho^* = 0.30$ ; (c)  $\rho^* = 0.05$ .

In order to avoid large correlations, an appropriate value for  $n_0$  has been obtained from the autocorrelation functions.

The autocorrelation functions for  $R^2$  and  $S^2$  are determined with the help of the general relationship

$$C_A(t) = \frac{\langle A(t_0)A(t_0+t) \rangle - \langle A(t_0) \rangle^2}{\langle A^2(t_0) \rangle - \langle A(t_0) \rangle^2}, \quad (9)$$

where  $A(t_0)$  is the value of  $R^2$  or  $S^2$  at time  $t_0$ . The data are averaged over  $t_0$ .

In Figs. 1 and 2 the autocorrelation functions for  $R^2$  and  $S^2$  are presented for several densities of the solvent.

The value of  $n_0$  is chosen such that  $C_{R^2}(n_0) < 0.10$ . An estimate of the standard deviations are obtained by dividing the samples into five groups and computing the standard deviations of the group averages. The results for several densities are shown in Table I.

The center-of-mass diffusion coefficient  $D$  can be obtained from the center-of-mass displacement or from the center-of-mass velocity autocorrelation function. These two methods proceed as follows:

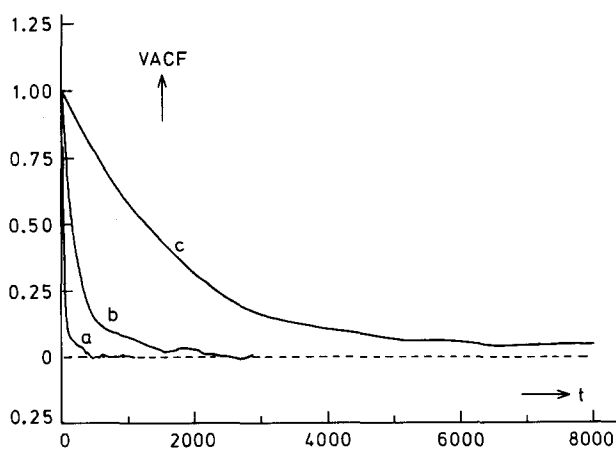


FIG. 4. Normalized velocity autocorrelation function. (a)  $\rho^* = 0.80$ ; (b)  $\rho^* = 0.30$ ; (c)  $\rho^* = 0.05$ .

TABLE II. The center-of-mass diffusion coefficient.  $D_a$  is obtained from the center-of-mass displacement and  $D_b$  from the center-of-mass velocity autocorrelation function.

$nr$	$\rho^*$	$D_a$	$D_b$
2	0.05	0.38	0.35
3	0.30	0.054	0.053
4	0.60	0.020	0.020
5	0.80	0.0094	0.0089

(a) By determining the limit value of the slope of the mean square center-of-mass displacement:

$$\lim_{t \rightarrow \infty} \langle \Delta Z^2(t) \rangle = 6Dt + C \quad (10)$$

with

$$\langle \Delta Z^2(t) \rangle = \frac{1}{N_T} \sum_{j=1}^{N_T} |\mathbf{Z}(j+t) - \mathbf{Z}(j)|^2. \quad (11)$$

We found that  $\Delta Z^2(t)$  rapidly approaches the asymptotic behavior as shown in Fig. 3.

(b) By the integration of the center-of-mass velocity autocorrelation function:

$$D = \frac{1}{3} \int_0^\infty dt \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle. \quad (12)$$

For several densities the normalized velocity autocorrelation function (VACF) is shown in Fig. 4.

We found that both methods gave consistent results which are given in Table II.

#### IV. CONCLUSIONS

In agreement with other molecular dynamics studies of polymer systems we found a large influence of the solvent on the dynamic properties of a star polymer. This is shown in Figs. 1 and 2 for the autocorrelation functions of  $R$  and  $S$  and in Table II for the center-of-mass diffusion coefficient  $D$ .

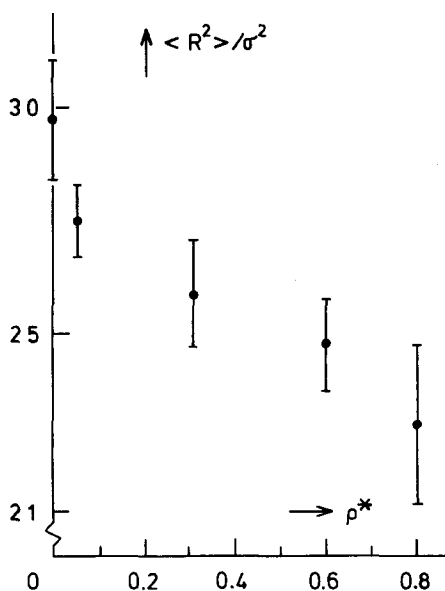


FIG. 5. The mean square end-to-end distance of the polymer as a function of the density.

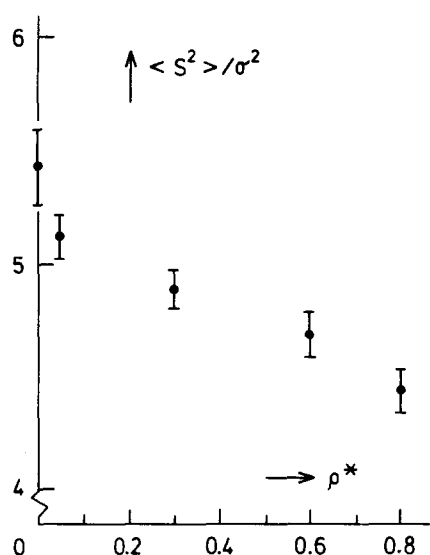


FIG. 6. The mean radius of gyration of the polymer as a function of the density.

According to our results the static properties of a star polymer are also influenced by the solvent as shown in Figs. 5 and 6. This is in contrast with the conclusion of Khalatur *et al.*<sup>9</sup> for linear polymers.

Although we proceeded with the simulation for about 40 times as long as Khalatur *et al.*<sup>9</sup> (at  $\rho^* = 0.8$ ), we obtained a larger statistical uncertainty in our results. In this respect it is important to note that in our study the time step between two samples is 20 000 times longer. It is not clear to what extent this large discrepancy can be due to the different

models adopted. These long correlation times for polymer systems were also observed in a recent study by Toxvaerd,<sup>15</sup> in which the Langevin equation was solved for these systems.

#### ACKNOWLEDGMENTS

The authors wish to acknowledge the contributions of M. Bishop and K. R. Cox.

<sup>1</sup>J. M. Prausnitz, *Molecular Thermodynamics of Fluid-Phase Equilibria* (Prentice-Hall, Englewood Cliffs, 1969).

<sup>2</sup>W. Bruns and R. Bansal, *J. Chem. Phys.* **74**, 2064 (1981).

<sup>3</sup>W. Bruns and R. Bansal, *J. Chem. Phys.* **75**, 5149 (1981).

<sup>4</sup>M. Bishop, M. H. Kalos, and H. L. Frisch, *J. Chem. Phys.* **70**, 1299 (1979).

<sup>5</sup>H. L. Frisch, M. Bishop, D. Ceperley, and M. H. Kalos, *J. Macromol. Sci. Phys. B* **18**, 453 (1980).

<sup>6</sup>M. Bishop, M. H. Kalos, and H. L. Frisch, *J. Chem. Phys.* **79**, 3500 (1983).

<sup>7</sup>D. C. Rapaport, *J. Chem. Phys.* **71**, 3299 (1979).

<sup>8</sup>D. C. Rapaport, *J. Phys. A* **11**, 1213, (1978).

<sup>9</sup>P. G. Khalatur, Yu. G. Papulov, and A. S. Pavlov, *Mol. Phys.* **58**, 887 (1986).

<sup>10</sup>M. Bishop and J. P. J. Michels, *J. Chem. Phys.* **82**, 1059 (1985), and references therein.

<sup>11</sup>H. G. A. Coorens, C. J. Peeters, and J. de Swaan Arons, Paper presented to the AIChE meeting, April 1987, Houston, Texas, and references therein.

<sup>12</sup>R. J. Needs and S. F. Edwards, *Macromolecules* **16**, 1492 (1983).

<sup>13</sup>K. E. Evans, *J. Chem. Soc. Faraday Trans. 2* **77**, 2385 (1981).

<sup>14</sup>L. Verlet, *Phys. Rev.* **159**, 98 (1967).

<sup>15</sup>S. Toxvaerd, *J. Chem. Phys.* **86**, 3667 (1987).